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⑦1 Anmelder:

Studiengesellschaft Kohle mbH, 45470 Mülheim,
DE

⑦4 Vertreter:

Patentanwälte von Kreisler, Selting, Werner, 50667
Köln

⑦2 Erfinder:

Reetz, Manfred T., Prof. Dr., 45470 Mülheim, DE;
Koch, Michael Georg, 45470 Mülheim, DE

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Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

⑤4 Wasserlösliche nanostrukturierte Metalloxid-Kolloide und Verfahren zu ihrer Herstellung

⑤7 Die vorliegende Erfindung betrifft mono-, bi- und mul-
timetallische, wasserlösliche Metalloxid-Kolloide, ein Ver-
fahren zu ihrer Darstellung sowie deren Trägerfixierung.
Das neue Verfahren ist gekennzeichnet durch die gezielte
Synthese von löslichen Metalloxid-Kolloiden mittels kon-
trollierter Hydrolyse der Edelmetallprecursor in Gegen-
wart eines wasserlöslichen Stabilisators. Diese Metall-
oxid-Kolloide können dann je nach Bedarf zu den entspre-
chenden Metallkolloiden reduziert werden. Die Trägerung
der Nanopartikel kann sowohl im Stadium der oxidierten
als auch der reduzierten Nanopartikel erfolgen.

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(71) Demandeur/Applicant:
STUDIENGESELLSCHAFT KOHLE MBH, DE
(72) Inventeurs/Inventors:
KOCH, MICHAEL GEORG, DE;
REETZ, MANFRED T., DE
(74) Agent: BERESKIN & PARR

(54) Titre : COLLOIDES D'OXYDE METALLIQUE NANOSTRUCTURES SOLUBLES DANS L'EAU ET PROCEDE PERMETTANT DE LES PRODUIRE

(54) Title: WATER-SOLUBLE NANOSTRUCTURED METAL-OXIDE COLLOIDS AND METHOD FOR PREPARING THE SAME

(57) Abrégé/Abstract:

The present invention relates to water-soluble, mono-, di- and multi-metallic metal-oxide colloids as well as to a method for representing the same and to their fixation on a carrier. This method is characterised in that the targeted synthesis of soluble metal-oxide colloids is achieved by the controlled hydrolysis of a noble metal precursor in the presence of a water-soluble stabiliser. The metal-oxide colloids can be reduced according to the needs into corresponding metal colloids. The fixation of the nanoparticles on the carrier can be carried out both at the oxidised state or reduced state of said nanoparticles.

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Abstract

The present invention relates to water-soluble, mono-, di- and multi-metallic metal-oxide colloids as well as to a method for preparing the same and to their fixation on a solid support. This method is characterized in that the targeted synthesis of soluble metal-oxide colloids is achieved by the controlled hydrolysis of a noble metal precursor in the presence of a water-soluble stabilizer. The metal-oxide colloids can be reduced according to the needs into corresponding metal colloids. The fixation of the nanoparticles on the solid support can be carried out both at the oxidized or reduced state of said nanoparticles.

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**Water-soluble Nanostructured Metal-Oxide Colloids
and Method for Preparing the same**

The present invention relates to mono-, bi- and multi metallic, water-soluble metal-oxide colloids, a method for preparing the same and their fixation on a support.

Nanostructured transition metal colloids are of great interest as catalysts for organic reactions, as electrocatalysts in fuel cells as well as structural elements in material science (G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994). In the literature, numerous chemical and physical processes for the preparation of metal colloids are known, e. g., the chemical reduction of common metal salts, as PdCl_2 , $\text{Pd}(\text{OAc})_2$, PtCl_4 , RuCl_3 , CoCl_2 , NiCl_2 , FeCl_2 or AuCl_3 , with a wide variety of reduction agents, the photolytical, radiolytical or thermal decomposition or reduction of appropriate metal precursors, or the method of metal vaporization. Recently, electrochemical methods for the preparation of metal colloids are being used too (M.T. Reetz, S.A. Quaiser, *Angew. Chem.* **1995**, 107, 2956; *Angew. Chem., Int. Ed. Engl.*, **1995**, 34, 2728). In order to prevent an undesired agglomeration of the nanoparticles into insoluble metal powders, stabilizers, such as ligands, polymers or surfactants are added in most cases (G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994).

Due to ecological and economical reasons water-soluble metal colloids are of particularly great interest in industry, the synthesis of which is ideal in an aqueous medium. The aim of preparing high concentrated,

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water-soluble, surfactant-stabilized metal colloids was achieved only in a few cases; however, the reduction step is relatively expensive or requires costly reduction agents, such as boron hydrides (M.T. Reetz et al., EP 0 672 765 A1, and H. Bönemann et al., DE 4 443 705 A1).

Furthermore, bimetallic nanoparticles are often clearly superior to the nanometallic species for certain catalytic applications, for which reason the selective synthesis of bimetallic metal colloids is gaining more and more in importance (G. Schmid, *Clusters and Colloids*, VCH, Weinheim, 1994).

Hereby, two different metal salts are chemically or electrochemically co-reduced in organic solvents in the presence of useful stabilizers, whereby the degree of alloy formation of the particles generally depends from the difference of the reduction potentials of the two metal salts used. Therefore, not all combinations of metals are possible by this route. The use of organic solvents and/or expensive reduction agents is also unfavorable.

Due to high polarity and high surface tension of the water, it is extremely difficult, just in an aqueous medium, to produce bimetallic colloids having a high degree of alloy formation. A special challenge also consists in alloying two metals which have a significantly different reduction potential, e.g., a noble metal, such as platinum, with a distinctly less noble metal, such as ruthenium, iron, cobalt or tin, in an aqueous medium in a way as simple as possible.

Now, a surprisingly simple solution to these problems could be achieved in an approach in which the metal salts are not reduced but condensed in an aqueous medium and in the presence of a water-soluble stabilizer,

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whereby the corresponding nano-structured metal oxide is formed. The stabilizer prevents the undesired formation and deposition, respectively, of insoluble metal oxide in bulk form. Working with two metal salts results in a co-condensation with formation of water-soluble colloidal bimetal oxides, whereby the size of the particles is also in the nanometer range.

The water-soluble metal-oxide colloids and bimetal-oxide colloids thus obtained can then be characterized with the aid of appropriate physical methods and can be processed to soluble or carrier-fixed catalysts. Hereby, the reduction of the colloidal metal oxide may take place with the help of reduction agents, such as hydrogen, hypophosphite or formate, without any appreciable change of the stoichiometry or of the particle size of the nanoparticles. The method allows an extension to trimetal oxides and multimetal oxides, respectively.

Contrary to the corresponding metal colloids, little is known in the literature about the preparation and the properties of metal oxide colloids of the late transitional metals. Henglein describes the preparation of colloidal MnO_2 by radiolysis of KMnO_4 (C. Lume-Pereira, et al., *J. Phys. Chem.* **1985**, 89, 5772), Grätzel (K. Kalyanasundaram, M. Grätzel, *Angew. Chem.* **1979**, 91, 759) as well as Harriman (P. A. Christensen, et al., *J. Chem. Soc., Faraday Trans.* **1984**, 80, 1451) obtained polymer-stabilized colloids of RuO_2 from RuO_4 or KRuO_4 , and Thomas reported colloids of IrO_2 by hydrolysis of H_2IrCl_6 in the presence of a polymer (A. Harriman, et al., *New J. Chem.* **1987**, 11, 757). Furthermore, publications by Nagy can be mentioned who obtained colloidal particles of ReO_2 in microemulsions by reduction of NaReO_4 with hydrazine (J. B. Nagy, A. Claerbout, in *Surfactants in Solution* (K. L. Mittal, D. O. Shah, Eds.), Plenum Press, New York, **1991**, p. 363; A.

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Claerbout, J. B. Nagy in *Preparation of Catalysts V* (G. Poncelet, Ed.), Elsevier, Amsterdam, **1991**, p. 705).

These colloidal oxides of noble metals must be distinguished from the publications of Matijevic, who describes metal oxides of metals, such as iron, aluminum, chromium, titanium, nickel and cerium, made by precipitation from homogenous solution (E. Matijevic, *Langmuir* **1994**, 10, 8; E. Matijevic, *Langmuir* **1986**, 2, 12), whereby the term of "colloidal" is not appropriate in this case, since the μm sized particles do not remain in solution in a colloidal form. Furthermore, colloidal metal oxides and metal sulfides may be mentioned, such as, for instance, CdS and CoFe_2O_4 , which usually are prepared in microemulsions and which are used in the semiconductor technology as well as in magnetic liquids (M. P. Pileni, *Langmuir* **1997**, 13, 3266).

Another possibility for preparing metal oxide colloids consists in oxidizing metal colloids afterwards in a specific manner, as could be shown in the case of electrochemically prepared nanoparticles of cobalt (M. T. Reetz, et al., *Angew. Chem.* **1996**, 108, 2228; *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2092); however, this method is not possible in water as a medium. Therefore, neither this method nor other methods are suitable for making available water-soluble nanoparticles of metal or bimetal oxides in an easy way.

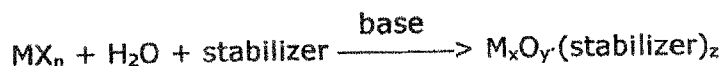
The new method of the controlled hydrolysis for preparing colloidal metal oxides and bimetal oxides has the following advantages:

- 1) Water as an inexpensive and ecologically benign solvent.
- 2) A nearly complete conversion of the metal precursors into soluble metal oxides or bimetal oxides (no loss of metal).

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- 3) Preparation of almost monodisperse nanoparticles in a size range of 0,5-5 nm, which means a high dispersion of the metals.
- 4) Simple purification and isolation of the colloid powders by dialysis and lyophilization.
- 5) Simple reduction of the metal oxides and bimetal oxides, respectively, by using hydrogen without any significant change of the stoichiometry and the size distribution.
- 6) Complete re-dispersibility of the colloid powder in water with concentrations of up to 0.5 mole of metal per liter of water.
- 7) Handling of the metal-oxide colloids in air without any difficulties, in contrast to the corresponding colloids of noble metals which are oxidized at the surface by air.
- 8) Fixation on a solid support at the stage of the oxidized species.
- 9) Control of the stoichiometry of the bimetals within a wide range.
- 10) Numerous water-soluble surfactants and polymers can be used as stabilizers.
- 11) The process may be extended to the preparation of trimetal oxide colloids and multimetal oxide colloids.

According to the invention, the aqueous solution or, if possible, the suspension of a salt of a transition metal or a mixture of two or more metal salts is treated with the aqueous solution of a base in the presence of a water-soluble stabilizer. This results in the hydrolysis of the metal salts and the condensation and co-condensation, respectively, with formation of colloidal monometal oxides or colloiddally alloyed mixed oxides.



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Scheme 1. Preparation of water-soluble metal-oxide colloids (MX_n = metal salt).

In the case of preparing monometal oxides, common salts of metals of the groups VIb, VIIb, VIII, Ib and IIb of the periodic table can be used as precursors. In the case of preparing colloidal bimetal oxides (mixed oxides), two common salts of metals of the groups VIb, VIIb, VIII, Ib and/or IIb of the periodic table are used and co-condensed, respectively; the same is possible when using one of these salts in combination with the salt of a metal from the main group of the periodic table, whereby, in particular, salts of tin may be used. In the case of preparing colloidal multimetal oxides, the corresponding mixtures consisting of three or more metal salts are chosen.

Carbonates, bicarbonates, hydroxides, phosphates or hydrogen phosphates of alkali metals and alkaline earth metals, such as LiOH, NaOH, KOH, $LiHCO_3$, $NaHCO_3$, $KHCO_3$, $CsHCO_3$, Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Cs_2CO_3 , $Mg(OH)_2$, $MgCO_3$, $CaCO_3$, Li_3PO_4 , Na_2HPO_4 , Na_3PO_4 or K_3PO_4 , serve as bases. Preferred bases are Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Cs_2CO_3 or $MgCO_3$.

Amphiphilic betains, cationic, anionic and nonionic surfactants or water-soluble polymers are possible as stabilizers. Typical examples of the amphiphilic betains are dimethyldodecylammoniopropane sulfonate and dimethyldodecylammoniopropane carboxylate, a typical example of the cationic surfactant is $[ClCH_2CH(OH)CH_2N(CH_3)_2C_{16}H_{37}]^+Cl^-$, a typical example of the anionic tenside is sodium cocoamidoethyl-N-hydroxyethyl glycinate, typical examples of the nonionic tensides are polyoxyethylenelauryl ether and polyoxyethylenesorbitanmono laurate, as well as typical examples of the water-soluble polymers are poly(vinyl

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pyrrolidone) (PVP), polyethylene glycol (PEG) or alkylpoly glycoside. It is also possible to use chiral water-soluble stabilizers such as poly-L-aspartic acid, sodium salt. The hydrolysis and condensation, respectively, of the metal salts in a basic, aqueous environment, and in the presence of a stabilizer is performed in a range of temperature of from 20 °C to 100 °C, preferably between 50 °C and 90 °C. Water serves as a solvent and at the same time as a chemical reactant, whereby the concentration of the aqueous solutions of the colloidal metal oxides can amount up to 0,5 M, in relation to the metal. However, mixtures of solvents, consisting of water and water-soluble organic solvent, can also be used.

The particle size of the nanostructured metal-oxide colloids is normally between 0,5 nm and 5 nm.

In the case of preparing bimetal-oxide colloids and of multimetal-oxide colloids, the mass ratio of the metals in the product can be controlled in an easy manner by the corresponding choice of the mass ratio of the metal salts. The colloidal metal oxides thus obtained as well as their reduction products with hydrogen can be characterized by means of numerous physical methods, such as HRTEM/EDX, XRD/DFA, XPS, EXAFS and UV spectroscopy.

For preparing heterogeneous catalysts starting from water-soluble colloids of metals and of metal oxides, numerous oxidic and nonoxidic solids, for example, Al_2O_3 , SiO_2 , CaCO_3 , MgO , La_2O_3 , carbon black or activated carbon, can be used as the solid support ("Trägerung").

For that purpose, an aqueous suspension of the solid support is treated with an aqueous solution of the metal colloids or of the metal oxide colloids, which causes the nanoparticles to be deposited on the solid

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support without any undesired agglomeration. It is also possible to carry out another kind of immobilization, for instance, the inclusion in sol-gel-materials by hydrolyzing $\text{Si}(\text{OCH}_3)_4$ or mixtures of $\text{Si}(\text{OCH}_3)_4$ and $\text{C}_n\text{H}_{2n+1}\text{Si}(\text{OCH}_3)_3$ ($n = 1-4$) in the presence of the metal-oxide colloids. With regard to the transformation of the nanoparticles of metal oxides into the corresponding nanoparticles of metals, the various reduction agents, particularly, hydrogen, sodium hypophosphite or sodium formate, are suited for this. The reduction may be done at the stage of the colloidal solutions of the metal oxides in water, or alternatively after the fixation on the solid support and the immobilization, respectively.

The colloids of metal, bimetals or multimetal oxides described herein can be applied as catalysts or precursors of catalysts for organic-chemical transformations, such as hydrogenations or oxidations. The application as electrocatalysts in fuel cells (e. g., Pt/Ru bimetal oxide) is also evident and of particular importance in view of the low production costs.

Example 1. PtRuO_x (3.12-SB)

370 mg (5 mmole) of Li_2CO_3 was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$ and 235.9 mg (1 mmole) of $\text{RuCl}_3 \times \text{H}_2\text{O}$ in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and of the condensation was followed by UV spectroscopy by means of the decrease of the H_2PtCl_6 absorption at 260 nm. After this

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band had completely disappeared, the reaction was terminated and cooled to room temperature. The colloidal solution was then filtered, in order to separate any precipitated metal oxide possibly present, and was submitted to an dialyzing process. Hereby, the colloidal metal oxide solution was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate monitored was conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 10.70 % Pt, 5.82 % Ru (this is corresponding to a molar ratio of 0,95:1)

TEM micrographs of the solution of the colloidal metal oxide solution show particles having a size distribution of $1.5 \pm 0,4$ nm. A individual-particle-EDX- analysis of these particles indicates bimetal character, since both metals always can be detected in a molar ratio between 1:2 and 2:1.

XPS examinations of these colloids showed that ruthenium is present in the oxidation state of IV, whereas two equal parts of platinum are incorporated into the colloid in the oxidation states of II and IV, respectively.

The XRD spectrum of the sample which was reduced in a stream of H_2 at 120 °C shows a scatter curve, from which an average peak distance of 2.73 Å can be calculated (bulk PtRu: 2.71 Å, bulk Pt: 2.774 Å, bulk Ru: 2.677 Å). As a result, the average particle size was found to be 1.2 nm. Principally, M_{13} -icosahedra as well as decahedra contribute to the DFA simulation of the scatter curve, whereas the proportion of larger particles of the fcc type being relatively small.

Example 2. PtRuO_x (1.12-CB)

370 mg (5 mmole) of Li₂CO₃ were weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0,1 M solution of dimethyldodecylammonio acetate (1-12-CB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 12.0 to a value of 8.5, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and the condensation were observed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. The colloidal solution was then filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of the conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 13.27 % Pt, 4,85 % Ru (this is corresponding to a molar ratio of 1.42:1)

TEM: 1.4 nm

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Example 3. PtRuO_x (PVP)

370 mg (5 mmole) of Li₂CO₃ as well as 3 g of poly(vinyl pyrrolidone) (PVP) were weighed in a 250 ml three-necked flask and dissolved in 80 ml of deionized water. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the polymer solution decreased from initially 11,5 to a value of 7,5, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and the condensation was monitored by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. Subsequently, the colloidal solution was filtered, in order to separate any precipitated metal oxide present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 2.9 g of a grey colloid powder was obtained which is completely re-dispersible in water, MeOH, EtOH and DMF.

Metal content: 6.78 % Pt, 3.15 % Ru (this is corresponding to a molar ratio of 1.11:1)

TEM: 1.6 nm

Example 4. PtRuO_x (3-12-SB), Pt/Ru = 4:1

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water

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was added thereto. A solution of 828.6 mg (1,6 mmole) of $\text{H}_2\text{PtCl}_6 \times 6 \text{H}_2\text{O}$ and 94.4 mg (0.4 mmole) of $\text{RuCl}_3 \times \text{H}_2\text{O}$ in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for ca. 6 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H_2PtCl_6 absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 14.87 % Pt, 2,97 % Ru (this is corresponding to a molar ratio of 2,59:1)

TEM: 1.5 nm

Example 5. PtRuO_x (3-12-SB), Pt/Ru = 1:4

370 mg (5 mmole) of Li_2CO_3 was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammoniopropane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 207.2 mg (0.4 mmole) of $\text{H}_2\text{PtCl}_6 \times 6 \text{H}_2\text{O}$ and 377.4 mg (1.6 mmole) of $\text{RuCl}_3 \times \text{H}_2\text{O}$ in 20 ml of deionized water was added dropwise thereto at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially

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11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for 6 hours, whereby the progress of the hydrolysis and the condensation was monitored by UV spectroscopy by means of the decrease of the H_2PtCl_6 absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 9.67 % Pt, 11.27 % Ru (this is corresponding to a molar ratio of 1:2.26)

TEM: 1.5 nm

Example 6. PtO_2 (3-12-SB)

296 mg (4 mmole) of Li_2CO_3 and 674 mg (2 mmole) of PtCl_4 were weighed in a 250 ml three-necked flask and dissolved in 160 ml of deionized water. 40 ml of a 0,1 M solution of dimethyldodecylammonio-propane sulfonate (3-12-SB) in deionized water was added thereto. The solution was stirred at 80 °C for 24 hours, whereby a discoloration from yellow orange to red brown occurred. After termination of the reaction, the colloidal platinum dioxide solution was filtered, and, subsequently, the solution was dialyzed twice against 1.5 l of deionized water in a Nadir dialyzing tube. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.3 g of a grey colloid powder was obtained which is completely re-dispersible in water.

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Metal content: 22.41 % Pt

TEM: 1.7 nm

Example 7. PtRuO_x-colloid having a chiral tenside as stabilizer

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0,1 M solution of 3-(N,N-dimethyldodecylammonio-2-(S)-hydroxy butyrate (3-12-CB*) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added thereto dropwise with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 12 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for 26 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.24 % Pt, 3.92 % Ru (this is corresponding to a molar ratio of 0.82:1)

TEM: 1.6 nm

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Example 8. PtRuO_x-colloid having a chiral polymer as stabilizer

37 mg (0.5 mmole) of Li₂CO₃ as well as 500 mg of poly-L-aspartic acid, sodium salt were weighed in a 50 ml two-necked flask and dissolved in 10 ml of deionized water. A solution of 51.8 mg (0.1 mmole) of H₂PtCl₆ x 6 H₂O and of 23.6 mg (0.1 mole) of RuCl₃ x H₂O in 5 ml of deionized water was added dropwise thereto with strong stirring over a period of 10 minutes at room temperature. Hereby, the pH value of the polymer solution decreased from initially 11,5 to a value of 7.5 after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for 26 hours. The progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. Subsequently, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 500 m g of a grey colloid powder was obtained which is completely re-dispersible in water, MeOH, EtOH and DMF. Metal content: 3.78 % Pt, 1.98 % Ru (this is corresponding to a molar ratio of 0.98:1)

TEM: 1.6 nm

Example 9. PtSnO_x (3-12-SB)

74 mg (1 mmole) of Li₂CO₃ as well as 103.6 mg (0.2 mmole) of H₂PtCl₆ x 6 H₂O were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0,1 M solution of dimethyldodecylammonio-

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propane sulfonate (3-12-SB) in deionized water. A solution of 37.8 mg (0.2 mmole) of $\text{SnCl}_2 \times 2\text{H}_2\text{O}$ in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H_2PtCl_6 absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0,5 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0,6 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.79 % Pt, 2.67 % Sn (this is corresponding to a molar ratio of 1.55:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

Example 10. PtFeO_x (3-12-SB)

74 mg (1 mmole) of Li_2CO_3 as well as 103.6 mg (0.2 mmole) of $\text{H}_2\text{PtCl}_6 \times 6 \text{H}_2\text{O}$ were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0,1 M solution of dimethyldodecyl-ammoniopropane sulfonate (3-12-SB) in deionized water. A solution of 39.8 mg (0.2 mmole) of $\text{FeCl}_2 \times 4 \text{H}_2\text{O}$ in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the

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decrease of the H_2PtCl_6 absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0,5 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0,6 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.12 % Pt, 1.24 % Fe (this is corresponding to a molar ratio of 1.42:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

Example 11. PtWO_x (3-12-SB)

74 mg (1 mmole) of Li_2CO_3 as well as 103.6 mg (0.2 mmole) of $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$ were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0,1 M solution of dimethyldodecyl-ammoniopropane sulfonate (3-12-SB) in deionized water. A solution of 66.0 mg (0.2 mmole) of Na_2WO_4 in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H_2PtCl_6 absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide present and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0,5 l of deionized water. The change of conductivity of the permeate was followed conductometrically.

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Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 4.61 % Pt, 0.78 % W (this is corresponding to a molar ratio of 5.5:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

Example 12. PtRuWO_x (3.12-SB)

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0,1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 141.5 mg (0.6 mmole) of RuCl₃ x H₂O and of 66.0 mg (0.2 mmole) of Na₂WO₄ in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 3 hours. Hereby, the pH value of the tenside solution decreased from initially 11.4 to a value of 9.8, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 22 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.8 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 8.31 % Pt, 2.91 % Ru, 0.73 % W

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TEM: 1.5 nm

Example 13: Reduction of the colloidal metal oxide solution

1 g of the isolated and purified PtRuO_x (3-12-SB) colloid prepared in accordance to example 1 was dissolved in 100 ml of deionized water in a Schlenk vessel under protective gas. After an ultrasonic treatment for 30 min, the Schlenk vessel was subjected to a slight evacuation for a short while, a gas balloon filled with hydrogen was connected therewith, and the solution was then stirred in a H₂ atmosphere at room temperature for 24 hours. The initially dark green to brown solution changes its color to deep black during this time. The colloidal solution can be lyophilized or can directly be processed on a carrier material for fixation.

TEM micrographs of the colloidal solution of PtRu show particles having a size distribution of $1,7 \pm 0,4$ nm. A EDX individual particle analysis of these particles indicates an almost complete formation of an alloy. XPS examinations with these colloids showed that both platinum and ruthenium are present in a metallic form.

Example 14: Fixation of a PtRu colloid on Vulcan as the solid support

3.552 g Vulcan XC-72R of the Cabot Company was weighed in a 1 l three-necked flask and suspended in 200 ml of a buffer solution (Citrate buffer, 50 mM, pH 4.7). 300 ml of an aqueous solution of PtRu(3-12-SB) (888 mg of noble metal) prepared according to specification of example 13 was added dropwise thereto under a protective gas at 50 °C for 3 hours. Subsequently, the suspension was stirred at 50 °C for 40 hours and stirred for another 16 hours at 100 °C. After cooling, the black suspension was centrifuged, the supernatant solution was decanted, the

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catalyst was washed twice with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 8.00 % Pt, 4.62 % Ru

Particle sizes: colloid without carrier: 2.2 ± 0.6 nm

colloid with carrier: 2.3 ± 0.6 nm

HRTEM micrographs of the catalyst show a homogenous distribution of the PtRu nanoparticles on the solid support.

Example 15: Fixation of a PtRuO_x colloid on Vulcan as the solid support

3.552 g Vulcan XC-72R of the Cabot Company which previously was surface oxidized with a solution of NaOCl was weighed in a 1 l three-necked flask and suspended in 200 ml of water. Then, 300 ml of an aqueous solution of PtRuO_x (3-12-SB) (888 mg of noble metal) prepared according to specification of example 1 was added dropwise thereto at 60 °C for 3 hours. Then, 0,1 M HCl was added dropwise there, until the solution reached a pH value of 2.5, and the suspension was stirred at 50 °C for 40 hours. After cooling, the black suspension was centrifuged, the supernatant solution was decanted, the catalyst was washed twice with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 14.32 % Pt, 8.45 % Ru

Example 16: Fixation of a PtRuO_x colloid on activated carbon as the solid support

5.7 g of activated carbon was weighed into a 500 ml three-necked flask and suspended in 200 ml of deionized water. 100 ml of an aqueous solution of PtRuO_x (3-12-SB) (300 mg of noble metal) which was prepared according to specification of example 1 was dropped thereto within 1 hour at 50 °C. Subsequently, the solution was stirred at 50 °C for 24 hours. After cooling and allowing to stand, the supernatant clear

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solution was decanted, the catalyst was washed three times with 200 ml methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 2.72 % Pt, 1.26 % Ru

Example 17: Fixation of a PtRu colloid on alumina as the solid support

5.7 g of Al_2O_3 was weighed in a 500 ml three-necked flask and suspended in 200 ml of deionized water. 100 ml of an aqueous solution of PtRu (3-12-SB) (300 mg of noble metal) prepared according to specification of example 13 was added dropwise thereto under a protective gas at 50 °C within 1 hour. Subsequently, the suspension was stirred at 50 °C for 24 hours. After cooling and allowing to stand, the catalyst was filtered, washed three times with 200 ml methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 2.91 % Pt, 1.70 % Ru

Example 18: Fixation of a PtRuO_x colloid on La_2O_3 as the solid support

5.7 g of La_2O_3 was weighed in a 500 ml three-necked flask and suspended in 200 ml of deionized water. 100 ml of an aqueous solution of PtRuO_x (3-12-SB) (300 mg of noble metal) prepared according to specification of example 1 was added dropwise thereto at 50 °C within 1 hour. Subsequently, the suspension was stirred at 50 °C for 24 hours. After cooling and allowing to stand, the catalyst was filtered, washed three times with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 2.83 % Pt, 1.88 % Ru

Example 19: Immobilization of a PtRuO_x colloid in sol-gel-materials

1.2 ml (8 mmole) of tetramethoxy silane (TMOS) was initially added to a 2 ml polypropylene vessel, and 0,5 ml of an aqueous solution of a PtRuO_x (3-12-SB) colloid (10 mg of noble metal; 20 g/l), prepared accor-

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ding to the specification of example 1, and 50 μ l of a 0,1 M solution of NaF was pipetted thereto. Subsequently, the vessel was sealed and agitated on a Vortex mixer at room temperature for 10 seconds. After a heating up has become evident, the black mixture was allowed to stand, whereupon a gelation of the solution occurred ca. 10 seconds later. Now, the gel was submitted to an ageing process in a sealed vessel at room temperature, for 24 hours and then dried at 37 °C in a drying oven for 3 days. To wash out the stabilizer, the gel was refluxed in 30 ml of ethanol for 3 days, centrifuged and washed again with 30 ml of ethanol, centrifuged again and finally dried in a drying oven at 37 °C for 4 days. 630 mg of a grey powder is obtained.

Metal content: 0.92 % Pt, 0.56 % Ru

Example 20: Hydrogenation of cinnamic ethyl ester

250 mg of a PtRuO_x/activated carbon (10 mg of noble metal) catalyst, prepared according to example 16, was weighed in a glass reactor which is equipped with a high speed stirrer. The reactor was sealed, connected to a thermostat and tempered to 25 °C. Following repeated processes of evacuation and argonization of the reactor, 60 ml of absolute methanol was added thereto, and the vessel was repeatedly evacuated for a short time at an agitator power of 2000 rpm. After stirring for 60 min in an atmosphere of H₂, 2 ml of cinnamic ethyl ester was injected, and the initial activity of the hydrogenation was determined by means of the time-dependant change of the H₂-level of the buret.

Activity: 150 ml of H₂/(g of noble metal·min). Under the same conditions, the classical Adams-catalyst showed a lower activity: 38 ml of H₂/(g of noble metal·min).

Claims

1. Water-soluble monometal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, made from metals of the groups VIb, VIIb, VIII, Ib or IIb of the periodic table, which are stabilized by water-soluble additives.
2. Water-soluble bi- and multimetal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, made from metals of the groups VIb, VIIb, VIII, Ib, IIb of the periodic table, which are stabilized by water-soluble additives.
3. Water-soluble bi- and multimetal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, made from a metal of the main group and from one or more metals of the groups VIb, VIIb, VIII, Ib, IIb of the periodic table, which are stabilized by water-soluble additives.
4. Colloids according to claim 3, wherein the metal of the main group of the periodic table is tin.
5. Colloids according to claims 1 - 4, wherein amphiphilic betains, cationic, anionic and nonionic surfactants or water-soluble polymers are used as water-soluble additives.
6. A process for producing additive-stabilized, water-soluble, mono-, bi- and multi metallic metal-oxide colloids having particle sizes in the range of 0.5 - 5 nm, characterized in that metal salts or mixtures of two or more metal salts are hydrolyzed or condensed

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or co-condensed, respectively, in basic aqueous solutions in the presence of a stabilizer in form of the additive.

7. The process according to claim 6, characterized in that salts of metals of the groups VIb, VIIb, VIII, Ib or IIb of the periodic table are hydrolyzed or condensed, respectively, in order to prepare water-soluble, monometallic metal-oxide colloids.
8. The process according to claim 6, characterized in that mixtures of two or more salts of metals of the groups VIb, VIIb, VIII, Ib and/or IIb of the periodic table are hydrolyzed or co-condensed, respectively, in order to prepare water-soluble, bi- or multi metallic metal-oxide colloids (mixed metal-oxide colloids).
9. The process according to claim 6, characterized in that mixtures of a salt of a metal of the groups VIb, VIIb, VIII, Ib or IIb and of a salt of a metal of a main group of the periodic table are hydrolyzed or co-condensed, respectively, in order to prepare water-soluble, bimetallic metal-oxide colloids.
10. The process according to claim 9, wherein the salt of a metal of a main group of the periodic table is SnCl_2 or SnCl_4 .
11. The process according to claims 6 - 10, wherein water-soluble amphiphilic betains, cationic, anionic or nonionic surfactants or water-soluble polymers are used as stabilizer in form of an additive.

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12. The process according to claims 6 - 11, wherein a carbonate, bicarbonate, a hydroxide, a phosphate or a hydrogen phosphate of an alkali metal or an alkaline earth metal is used as a base.
13. The process according to claim 12, wherein Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Cs_2CO_3 or MgCO_3 are used as a base.
14. The process according to claims 6 - 13, characterized in that the reaction temperature is between 20 and 100 °C, preferably, between 50 and 90 °C.
15. The process according to claims 6 and 8 to 14, characterized in that the mass ratio of the metals in the bi- or multi metallic metal-oxide colloids is controlled by the corresponding choice of the mass ratio of the metal salts.
16. The process for preparing water-soluble, nanostructured, mono-, bi- and multi metallic metal colloids having particle sizes of 0,5 nm to 5 nm, characterized in that the corresponding metal-oxide colloids can be produced according to the claims 6 to 15 and subsequently be reduced.
17. The process according to claim 16, wherein hydrogen, hypophosphite or formate are used as a reduction agent.
18. The process for fixation of the metal-oxide colloids prepared according to the claims 1 to 5, and of the metal-oxide colloids which are prepared therefrom according to the claims 16 to 17 on solid supports, characterized in that solid oxidic or non oxidic solid materials are treated with aqueous solutions of the colloids.

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19. The process for immobilization of the metal-oxide colloids which are prepared according to the claims 1 to 5, and of the metal-oxide colloids which are prepared therefrom according to the claims 16 to 17, characterized in that they are incorporated in sol-gel-materials.
20. The process according to claim 19, wherein sol-gel-materials are used, for which $\text{Si}(\text{OCH}_3)_4$ or mixtures of $\text{Si}(\text{OCH}_3)_4$ and $\text{C}_n\text{H}_{2n+1}\text{Si}(\text{OCH}_3)_3$ ($n = 1$ to 4) are used as gel precursors.



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European Patent Office
Postbus 5818
2280 HV RIJNSWIJK
NETHERLANDS
Tel. +31 (0)70 340-2040
Fax +31 (0)70 340-3016



von Kreisler, Alek
Patentanwälte
von Kreisler-Selting-Werner
Postfach 10 22 41
D-50462 Köln
ALLEMAGNE

For any questions about
this communication:
Tel.: +31 (0)70 340 45 00

Date
23.02.09

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Applicant/Proprietor Asahi Kasei Medical Co., Ltd.	

Communication

The European Patent Office herewith transmits as an enclosure the supplementary European search report under Article 153(7) EPC for the above-mentioned European patent application.

If applicable, copies of the documents cited in the European search report are attached.

- ☒ 1 additional set(s) of copies of the documents cited in the European search report is (are) enclosed as well.

Refund of the search fee

If applicable under Article 9 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.



**SUPPLEMENTARY
PARTIAL EUROPEAN SEARCH REPORT**

Application Number

which under Rule 63 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 198 03 891 A1 (BAYER AG [DE]) 5 August 1999 (1999-08-05) * abstract * * column 1, line 59 - column 3, line 55 * * column 4, line 20 - line 22 * * claims 1,2,4-9; examples 1,2 *	1,6,7, 11,12, 15-18	INV. B22F9/24 B01D65/10 B01J13/00 G01N15/08
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X	WO 02/087749 A (POSTECH FOUNDATION [KR]; LEE MU-SANG [KR]; NAM SANG-IL [KR]; MIN EUN-S) 7 November 2002 (2002-11-07) * page 2, line 29 - page 3, line 19 * * page 3, line 29 - page 5, line 30 * * page 6, line 15 - page 7, line 4 * * page 7, line 26 - page 9, line 4 *	1,6,7, 11,12, 15-18	
The supplementary search report has been based on the last set of claims valid and available at the start of the search.			TECHNICAL FIELDS SEARCHED (IPC)
INCOMPLETE SEARCH			A61K B22F B01D B01J
<p>The Search Division considers that the present application, or some or all of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for the following claims:</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
2	Place of search The Hague	Date of completion of the search 9 February 2009	Examiner Ceulemans, Judy
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>..... & : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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